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(54) Sulphur dyes as polymer antioxidants

(57) A sulphur dye in solid form is used as an antioxidant in a polymeric material.

The dye e.g. C. I. Sulphur Brown 96 may be incorporated by a masterbatch technique.

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Improvements in or relating to organic compounds

The invention relates to the use of sulphur dyes as antioxidants in polymeric materials, especially polyolefins.

Many types of antioxidants are known. One of the more common phenolic antioxidants on the market is tetrakis [methylene-3(3',5'-di tert. butyl-4'-hydroxyphenyl)propionate] methane, sold (for example) as "Irganox" 1010 (a Trademark) (hereinafter "TMBP").

It has surprisingly been found that sulphur dyes, in the stable oxidised form (and not in leuco form), act as very good antioxidants; indeed they can act more effectively than TMBP in some instances.

According to the invention there is provided the use of sulphur dye preferably in solid form as an antioxidant in a polymeric material.

It is essential that the sulphur dye used in the invention is not in reduced form (i.e. not in the leuco sulphur dye form but rather in the oxidised form).

Further, according to the invention there is provided a masterbatch composition (hereinafter defined as the masterbatch) comprising a polymeric material and an antioxidant, which is a sulphur dye.

Preferably the sulphur dye is present in the masterbatch in a concentration of 5-40%, more preferably 5-20%, more preferably about 10%, by weight.

Preferably the sulphur dye used is micronised, preferably having an average size of 1 to 10 microns.

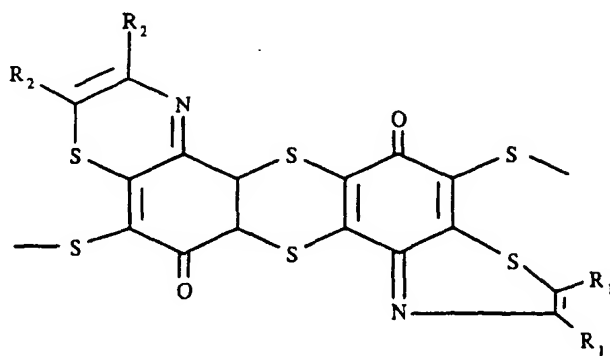
For the avoidance of doubt, sulphur dyes, alternatively known as sulphurised Vat dyes are well known in the art and are, for example, defined in VENKATARAMEN "The Chemistry of Synthetic Dyes" Vol II (Chapters XXXV and XXXVI) (1952) and Vol. VII (1974) or as defined in the "Colour Index" as "Sulphur Dyes" and also as "VAT dyes" with the further indication sulphur and with a structure number and/or a synthetic method involving a sulphurisation. Essentially they are dyes that contain aromatically bound oligosulphide bridges that are reducible to thiol groups and may optionally be of oligomeric to polymeric structure. They are essentially free of any solubilising sulpho groups (and also free of any thiosulphonic acid groups).

Sulphur dyes that can preferably be used are those selected from:

- C. I. Sulphur Black 1
- C. I. Sulphur Black 2
- C. I. Sulphur Black 11
- C. I. Sulphur Black 18
- C. I. Sulphur Red 10
- C. I. Sulphur Red 14
- C. I. Sulphur Blue 3
- C. I. Sulphur Blue 7
- C. I. Sulphur Blue 11
- C. I. Sulphur Blue 13
- C. I. Sulphur Blue 15
- C. I. Sulphur Blue 20
- C. I. Vat Blue 43
- C. I. Sulphur Green 2
- C. I. Sulphur Green 16

C. I. Sulphur Green 35
C. I. Sulphur Green 36
C. I. Sulphur Brown 1
C. I. Sulphur Brown 3
C. I. Sulphur Brown 10
C. I. Sulphur Brown 21
C. I. Sulphur Brown 26
C. I. Sulphur Brown 31
C. I. Sulphur Brown 37
C. I. Sulphur Brown 52
C. I. Sulphur Brown 95
C. I. Sulphur Brown 96
C. I. Sulphur Orange 1
C. I. Sulphur Yellow 9
C. I. Sulphur Yellow 22

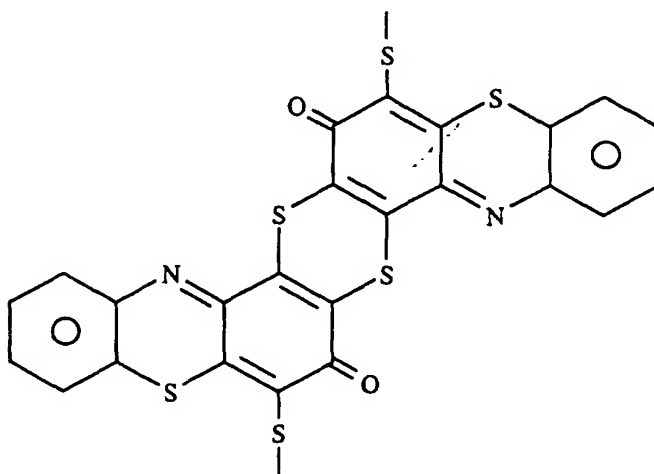
More preferred sulphur dyes are those containing 1-10 units, which said unit contains a group of the formula



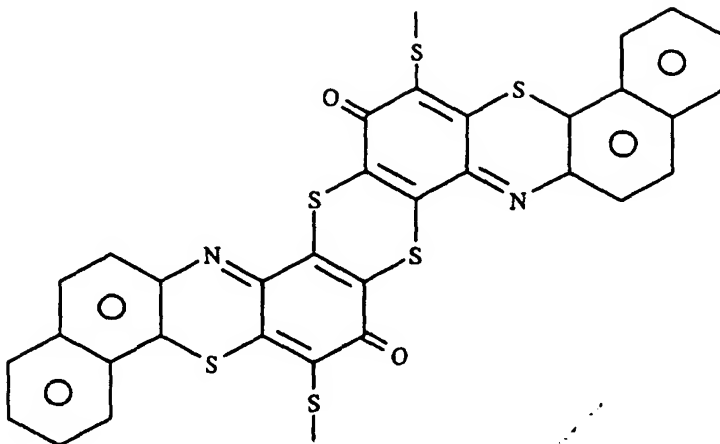
in which both groups R_1 and both groups R_2 together with the carbon atoms to which they are attached form a phenyl or naphthyl group.

Most preferred sulphur dyes are those containing 1 to 10 recurring units of formula 1 or 2

(1)



(2)



Of the sulphur dyes that can be used in the present invention, C.I. Sulphur Brown 96, C. I. Sulphur Black 11, C.I. Sulphur Black 11 and C.I. Sulphur Green 16 are especially preferred. A more especially preferred sulphur dye for use in the present invention is C.I. Sulphur Brown 96.

Still further according to the invention, there is provided a process for stabilising against the effects of heat, light and oxygen (e.g. against weathering conditions) a polymeric material comprising adding to the polymeric material a stabilising quantity of a sulfur dye as hereinabove defined or a masterbatch containing such a stabilising quantity.

Preferably a stabilising amount is 0.005 to 5% based on the polymeric material to be stabilised.

Suitable polymeric materials are polyolefins, polyamides, polycarbonate, acrylonitrile-butadiene-styrene-copolymers, polystyrol, styrol-acrylonitrile-copolymers, high impact polystyrene, polyester, polyesterketones and polyethersulfones.

Preferred polymeric materials are polyolefins such as polyethylene (e.g. high density polyethylene, low density polyethylene, linear low density polyethylene, or medium density polyethylene), polybutylene, poly-4-methylpentene and copolymers thereof.

More preferred polymeric materials are polyolefins and their copolymers prepared by using processing catalysts known as Generation I to Generation V catalysts and which may or may have not (preferably have not) been subjected to a catalyst removal step.

By the term "catalyst removal step" is meant a step which comprises, for the purpose of positively removing the catalyst residue contained in the polymerized polyolefins, treating the polyolefins with compounds which can react with the catalyst residue and inactivate or solubilize the residue, for example alcohols or water, and then removing the inactivated or solubilized catalyst residue by physical means such as filtration, washing, and centrifuging.

Thus, in the case of suspension polymerization, the step of separating the resulting polymer from a dispersion medium such as a solvent or a liquified monomer does not fall under the above-mentioned definition of the catalyst residue-removal step, although the catalyst dissolved in the dispersion medium may be removed at the separation step. The step of adding a small amount of catalyst poisons such as ethers, alcohols, ketones, esters and water to the resulting polymer suspension with a gas such as steam or nitrogen to remove the dispersion medium also does not fall under the above-mentioned definition of the catalyst residue-removal step.

What is meant by Generation I catalysts is titanium halide catalysts and an organo aluminium compound or an organo aluminium halide.

What is meant by Generation II catalysts is Generation I catalysts supported on an organo magnesium compound or based on an organo chromium compound supported on SiO_2 .

What is meant by a Generation III catalyst is a Ziegler-type complex catalyst supported on a halogen-containing magnesium compound.

What is meant by a Generation IV catalyst is a Generation III catalyst with a silane donor.

What is meant by a Generation V catalyst is a bis-indenyl organo titanium compound supported on alumoxane or is a bis-cyclopentadienyl-titanium halide activated by aluminium alkyl compounds.

Further generations of highly specific catalysts, especially useful for manufacturing highly stereoregular polyolefins, which are presently under development also belong, in the sense of the present invention, to the aforementioned generations of supported catalyst systems. Examples of such highly stereoregular polyolefins are syndiotactic polypropylene, isotactic stereoblock polymers, isotactic polypropylene containing steric defects distributed along the polymer chain (so called anisotactic polypropylene) or stereoirregular stereoblock polymers.

Because of the rapid progress in the development of supported newer generation catalyst systems (eg the metallocene catalysts), the commercial significance of these polymers with novel, highly-interesting properties is steadily increasing. However, residues of such further catalyst generations, can also cause disadvantageous properties in the polymer, if they contain metals of the 3d, 4d and 5d series of the periodic system supported analogously to the earlier catalyst generations, and if such residues are not removed physically and are still present in the polymer even in a deactivated form.

These Generations of Catalysts are described in the Twelfth Annual International Conference on Advances in the Stabilization and Controlled Degradation of Polymers, held in Luzern, Switzerland, 21-23 May 1990 in an article on pages 181 to 196 inclusive by Rolf Mülhaupt entitled "New Trends in Polyolefin Catalysts and Influence on Polymer Stability".

The contents of this article is incorporated herein by reference and especially Table I on page 184 describing the Generation of Catalysts:

TABLE I Polyolefin Catalyst Evolution

Generation Example	Cat.Act. (gPP/gTi h atm)	% Act.Ti	Stereoreg. (% hept.ins.)	Process Technology
I. $\text{TiCl}_4/\text{AlR}_3$	40	0.01	45%	removal of cat.residues and atactic PP
$\text{TiCl}_3/\text{AlEt}_2\text{Cl}$	30	0.1	92%	removal of catalyst residues
II $\text{Mg}(\text{OEt}_2)/\text{TiCl}_4/\text{AlR}_3$ $\text{SiO}_2/\text{Cp}_2\text{Cr}$	40000 40000	HDPE	50%	no removal of cat.residues (mainly HDPE/LLDPE)
III Mod. TiCl_3 cat. $\text{MgCl}_2/\text{TiCl}_4/\text{AlR}_3$ +ester donor	5000 20000	1 10	95% 92%	no purification
IV $\text{MgCl}_2/\text{TiCl}_4/\text{AlR}_3$ +silane donor	40000	18	99%	no purification no extrusion
V Bis-indenyl- TiR_2 on $(\text{AlCH}_3\text{O})_2$	40000	100	99%	novel PPs, narrow MWD

in which R is an organo group; HDPE is high density polyethylene, LLDPE is linear low density polyethylene, Cp is cyclopentadienyl, Et is ethyl, PP is polypropylene and MWD is molecular weight distribution.

A masterbatch according to the invention may be added before, during or after the polymerization step and may be added in solid or molten form, in solution, preferably as a liquid concentrate containing from 10 to 80% by weight of the composition and 90 to 20% by weight of a solvent, or as a solid masterbatch composition containing 10 to 80% (more preferably 40 to 70%) by weight of the composition and 90 to 20% (more preferably 60 to 30%) by weight of a solid polymeric material which is identical or compatible with the material to be stabilized.

Of particular importance is blending the masterbatch in the melt with the polymeric material to be stabilised.

The oxidised sulphur dye may be incorporated by known methods into the polymeric material to be stabilized. Such methods include a dry-blending of the sulphur dye with the polymer fluff. Of particular importance is the blending of the sulphur dye in the melt, for example in a melt blender or during the formation of shaped articles, including foils, films, tubes, containers, bottles, fibres and foams by extrusion, injection moulding, blow moulding, roto-moulding, spinning or wire coating. The use of sulphur dye alone or in the masterbatch according to the invention are particularly preferred in polypropylene and polyethylene articles of every type.

Other antioxidants may be added to polymeric material either before, at the same time as or after (but before polymerisation occurs) the addition of a composition according to the invention.

Examples of suitable further antioxidants include benzofuran-2-ones, indolin-2-ones, sulphur and phosphorus containing compounds and mixtures thereof.

Preferred sulphur - containing antioxidative co-stabilisers which may be used include di-tridecyl--3,3-thiodipropionate, distearyl-3,3-thiodipropionate, di-lauryl-3,3-thiodipropionate, methane tetrakis (methylene-3-hexyl-thiopropionate), methane tetrakis (methylene-3-dodecylthiopropionate) and dioctadecyl disulphide.

Preferred phosphorus-containing co-stabilizers which may be used include trinonylphenyl phosphite, 4,9-distearyl-3,5,8,10-tetraoxa-diphosphaspirodecane, tris- (2,4-ditert.butyl-phenyl) phosphite, triauryl phosphite, bis(2,6-di-t.butyl-4-methylphenyl)pentaerythrityl -diphosphite, bis(2,4-di-t.butylphenyl)pentaerythrityl-diphosphite, distearyl pentaerythrityl diphosphite and tetrakis-(2,4-ditert.butylphenyl)-4,4'-biphenylene diphosphonite.

Other additives which may be added to polymeric compositions according to the invention include aminoaryl compounds, U.V. stabilisers and antistatic agents, flameproofing agents, softeners, plasticisers, lubricants, guard agents, complexants, nucleating agents, metal deactivators, biocides, impact modifiers, fillers, pigments and fungicides.

Preferred aminoaryl compounds include N,N'-dinaphthyl-p-phenylene diamine and N,N'-hexamethylene-bis-3-(3,5- ditert.butyl-4-hydroxy phenyl)- propionamide.

Preferred U.V. stabilisers include U.V. absorbers (e.g. 2-(2'-hydroxyphenyl)- benzotriazoles, 2-hydroxybenzophenones, 2-hydroxyphenyl-1,3,5-triazines 1,3-bis-(2'-hydroxybenzoyl-) benzene salicylates, cinnamates and oxalic acid diamides; U.V. quenchers such as benzoates and substituted benzoates; and hindered amine light stabilisers (for example N-unsubstituted, N-alkyl or N-acyl substituted 2,2,6,6-tetra-alkyl piperidine compounds).

Such additives are described in "Kunststoffe Additive" Gächter/Müller, 3rd Ed. 1990 pp. 42-50, the contents of which are incorporated herein by reference. See page 4 last two lines for this.

The invention will now be illustrated by the following Example in which all parts and percentages are by weight and all temperatures are in °C.

Example

90 parts of a low density polyethylene in powder form commercially available as Escorene (Exxon), is mixed together for 4-5 minutes in a turbomixer with 10 parts of finely micronised C.I. Sulphur Brown 96 (having an average size of 1-5 microns)

After this, the mixture is predispersed in a TRAF Brabender at 140 revs/min for 3 seconds. The resulting masterbatch is added at a concentration of 0.05% to polypropylene, commercially available as Moplen from Himont. This is then extruded five times, measuring MFI (melt flow index) after each passage.

Other commercially available polyethylene that can be used in place of Escorene in the Example are: - PE 022 GRADO 70 from Repsal, Stamylan LD from DSM and Riblene from Enichem.

Other commercially available polypropylene that can be used in place of Moplen in the Example are: - Propatene from ICI, Eltex from Solvay and SM from Shell.

The Example is repeated using 0.05% of C.I. Sulphur Black 1, C.I. Sulphur Black 11 and C.I. Sulphur Green 16. The results are as follows:

Stabilization Test for Polypropylene

Measurement: M.F. I. 230°C - 2,160 kg after passages in Extruder Brabender at 260°C

Type of Polymere	Stabilizator	Number of Passages						Delta% 5/0	Delta% 5/1
		0	1	2	3	4	5		
PP FL/F 20 (GR.12)	1) -	12.0	15.6	16.0	16.4	19.2	22.6	88.3	44.9
PP FL/F 20 (GR.12)	2) 0.1% IRGANOX 1010	12.0	13.5	14.1	14.5	15.8	16.3	35.8	20.7
PP FL/F 20 (GR.12)	Sulphur Brown 96	12.0	13.1	14.0	14.6	15.4	16.3	35.8	24.4
PP FL/F 20 (GR.12)	Sulphur Black 1	12.0	14.5	15.6	16.3	18.2	19.6	63.3	35.2
PP FL/F 20 (GR.12)	Sulphur Black 11	12.0	11.9	12.9	13.5	14.7	15.2	26.7	27.7
PP FL/F 20 (GR.12)	Sulphur Green 16	12.0	13.7	14.8	13.8	14.7	17.5	45.8	27.7

PP FL/F 20 (GR 12) is a polypropylene commercially available as Moplen.

Claims

1. The use of a sulphur dye in solid form as an antioxidant in a polymeric material.
2. The use according to claim 1 of C.I. Sulphur Brown 96.
3. A masterbatch composition comprising a polymeric material and an antioxidant which is a sulphur dye.
4. A masterbatch according to Claim 3 in which the sulphur dye is C.I. Sulphur Brown 96.
5. A masterbatch substantially as herein described with reference to the Example.